TDMA

TITANIUM DIOXIDE MANUFACTURERS ASSOCIATION

for a brighter future

Interpretation of the harmonised classification of titanium dioxide (TiO_2)

European Union Classification and Labeling (CLP) Regulation

10 September 2021

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1.0 Introduction

The European Commission has classified certain forms of titanium dioxide (TiO_2) as a category 2 carcinogen by inhalation according to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures[1]. This means that certain forms of TiO_2 and mixtures containing these forms of TiO_2 may require special labelling. These requirements will apply from 1 October 2021.

The new entry for TiO_2 in Annex VI of the CLP is much more complex than typical entries in the CLP as the classification is limited to inhalation, accompanied by several specific notes intended to limit its scope, and has terminology which is new under the CLP. It is also ambiguous and can be subject to multiple interpretations.

The objective of this guidance is to provide the TDMA's interpretation of the scope and application of the TiO_2 harmonised classification and to help to the best extent possible the manufacturers, importers and downstream users in applying this classification.

Many experts and organizations including TDMA do not agree with the classification of TiO_2 as category 2 carcinogen. There is no evidence of lung cancer in humans, even in the most exposed workers, and the evidence relied on by the European Commission is mainly based on a single study with rats, that were exposed to extremely high concentrations, causing significant impairment of particle clearance mechanisms in the lungs (excessive overload). The observed rat tumours were a confounding effect due to such excessive overload, unrelated to the TiO_2 intrinsic property to cause cancer. Note W of the classification makes reference to this significant impairment (but it does not provide any clarification as to how should this be applied or taken into account by the manufacturers, importers and downstream users of TiO_2).

In addition, many experts and organizations, including TDMA, considers that the classification of TiO_2 is legally questionable for several reasons, including the CLP criteria for classification and the proportionality of the classification. In view of all this, the members of TDMA and other companies are challenging the Commission's decision to classify TiO_2 before the General Court of the European Union.

Though not covered in this guidance, it is recommended to continue common practice for occupation safety measures to reduce dust exposure for workers.

Waste, toys and cosmetics - The classification has implications for these areas. Though not covered in this guidance, the recommendations may be helpful in the interpretation of the classification in these applications.

[1] Commission Regulation (EU) 2020/217 - 14th ATP of CLP

2.0 Classification entry

The entry in different sections of Regulation (EC) No 1272/2008 are shown below.

Annex VI Listing

Index No	Chemical Name	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors	Notes
				Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	Suppl. Haz. State. Code(s)		
022-006-002	titanium dioxide; [in powder form containing 1% or more of particles with aerodynamic diameter ≤ 10 µm]	236-675-5	13463-67-7	Carc. 2	H351 (inhalation)	GHS08 Wng	H351 (inhalation)			V, W, 10

Labelling pictogram	GHS08	 Warning
Hazard statement	H351 (inhalation)	Suspected of causing cancer (inhalation)

Annex III – Notes

Note V:

If the substance is to be placed on the market as fibres (with diameter < 3 µm, length > 5 µm and aspect ratio ≥ 3:1) or particles of the substance fulfilling the WHO fibre criteria or as particles with modified surface chemistry, their hazardous properties must be evaluated in accordance with Title II of this Regulation, to assess whether a higher category (Carc. 1B or 1A) and/or additional routes of exposure (oral or dermal) should be applied

Note W:

It has been observed that the carcinogenic hazard of this substance arises when respirable dust is inhaled in quantities leading to significant impairment of particle clearance mechanisms in the lung.

This note aims to describe the particular toxicity of the substance; it does not constitute a criterion for classification according to this Regulation.

Note 10:

The classification as a carcinogen by inhalation applies only to mixtures in powder form containing 1% or more of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.

3.0 Application of the classification

3.1 TiO_2 powder

TiO_2 powder will be classified when it contains 1% or more of particles with an aerodynamic diameter less than 10µm and therefore is expected to be classified. Methods to determine this fraction are shown in Section 5.0. Many grades of TiO_2 do not meet the criteria for classification as the particles are bound together in agglomerates which have an aerodynamic diameter greater than 10µm. Further information is provided in Section

In the absence of specification in the TiO_2 entry, this interpretation presumes that different crystal forms of TiO_2 such as rutile and anatase are similar and are covered by the same classification. Even though only a single EC and CAS number is included in the entry, other EC and CAS numbers could also covered by such generic number.

	EC Number	CAS Number
Titanium dioxide (TiO2)	236-675-5	13463-67-7
Rutile (TiO2)	215-282-2	1317-80-2
Anatase (TiO2)	215-280-1	1317-70-0

3.2 Liquid mixtures

The classification only applies to mixtures in powder form, so therefore any liquid mixture containing TiO_2, regardless of the concentration, is not classified according to Note 10, unless the mixture contains other hazardous substances that trigger classification. TiO_2 is insoluble so normally exists in a liquid mixture as an emulsion, suspension, liquid dispersion or a slurry in water. However, these can be considered as liquid mixtures and should not be classified. Some TiO_2 is also placed on the market in water slurry form and therefore would not be classified. Some liquid mixtures may require Annex II labels, see Section 4.0.

3.3 Gaseous mixtures

In theory, gaseous mixtures are also excluded from classification, though TDMA is not aware of any TiO_2 placed on the market in that form.

3.4 Solid mixtures

A powder is considered a solid in the CLP, as it does not meet the definitions of liquid or gas. The CLP also states that solids can include granules, flakes, pellets and powders. A solid mixture is only classified when it is in powder form unless the mixture contains other hazardous substances. Some solid mixtures may require Annex II labels, see Section 4.0.

3.5 Powder form

The term "powder" is a critical identifier in the classification of TiO_2. However, there is no definition of powder in the CLP or other EU legislation or standards regulating chemicals, though some entries in CLP include a reference to "powder". This creates uncertainty as different interpretations could be applied.

This interpretation considers that the powder is a dry bulk solid that is normally free flowing when shaken or tilted. CLP entries for lead powder and nickel powder include a particle diameter of < 1 mm. ISO 3252 (2019) - Powder metallurgy – Vocabulary defines a powder as particles that are usually less than 1 mm in size.

A solid that is clumped and caked, which is typically due to moisture and wetting, is generally not in powder form. Visual inspection may be sufficient to determine if a substance is in powder form. Solid mixtures such as polymer pellets are not in powder form and therefore can be excluded from classification.

3.6 Determining if a powder is classified

A substance or mixture will only be classified if it contains 1% or more of TiO_2 which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm as detailed in Note 10.

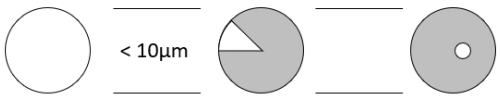


Figure 1: Illustration of different cases. Only the white area is considered within the 1% or more of TiO_2.

For a powder mixture that is made by blending TiO_2 powder with another powder not containing TiO_2, this can be determined by simple calculation with the characteristics of the TiO_2 powder used as an ingredient in the mixture. In other cases, this can be quite difficult to determine and therefore it is recommended to do a staged approach as shown in Figure 2. Section 7.0 contains some theoretical examples of determining this.

The aerodynamic diameter must be determined in air. A definition of the aerodynamic diameter is included in Section 5.1 and a recommended methodology to determine the content of particles less than 10µm in included in Section 5.2.

It should be established if the TiO_2 is evenly dispersed through all particle sizes or has a higher concentration in particles smaller or larger than an aerodynamic diameter of 10 µm. If the TiO_2 content of the particles with aerodynamic diameter ≤ 10 µm is unknown, the content of TiO_2 in substance or mixture can be determined as described in Section 3.7.

The entry does not make reference to weight, but virtually all references, except gaseous mixtures, in CLP refer to the percentage on a weight basis (% wt. or % w/w). This includes the specific and generic concentration limits (SCL, GCL) as well as multiple entries in Annex VI including content and particle size. Though not specified in the entry for TiO_2, this guidance works on the basis that all percentages including content in liquid mixtures and particles less than 10µm are on a weight basis.

3.7 Determining the TiO_2 content of solids

The TiO_2 content of solids can be determined in the following ways:

- Digestion in suitable acid and then analysis of the liquid solution for titanium (Ti) metal by methods such as inductively coupled plasma (ICP).
- X-ray fluorescence (XRF) for direct analysis of the titanium (Ti) metal in a solid, which avoids digestion but requires calibration.

If it is known that the Ti is in dioxide form, the TiO_2 content can be calculated the ratio of molecular weight (x 1.67).

3.8 Chemical form of titanium

TiO_2 is inert and insoluble and will remain in the TiO_2 chemical form unless it undergoes vigorous chemical or thermal treatment. For example, where TiO_2 is directly added as a pigment to a solid matrix such as plastic, it is expected that the TiO_2 will remain in the dioxide form.

Many ores, minerals and residues contain titanium and it is often assumed that it is in the dioxide form. The content of the titanium element is much easier to determine than the chemical form. If the titanium chemical form is unknown, it is recommended to determine the content of Ti as described in Section 3.7 and then the form according to a method such as X-ray diffraction (XRD).

Hydrate forms of TiO_2, mono-hydrate $TiO_2.H_2O$ and titanium dihydrate $TiO_2.2H_2O$ are considered within the scope of the same entry and should not be differentiated under CLP. The H_2O molecules in the hydrate forms should not be used in the determination of the % wt. of TiO_2 in the substance or mixture.

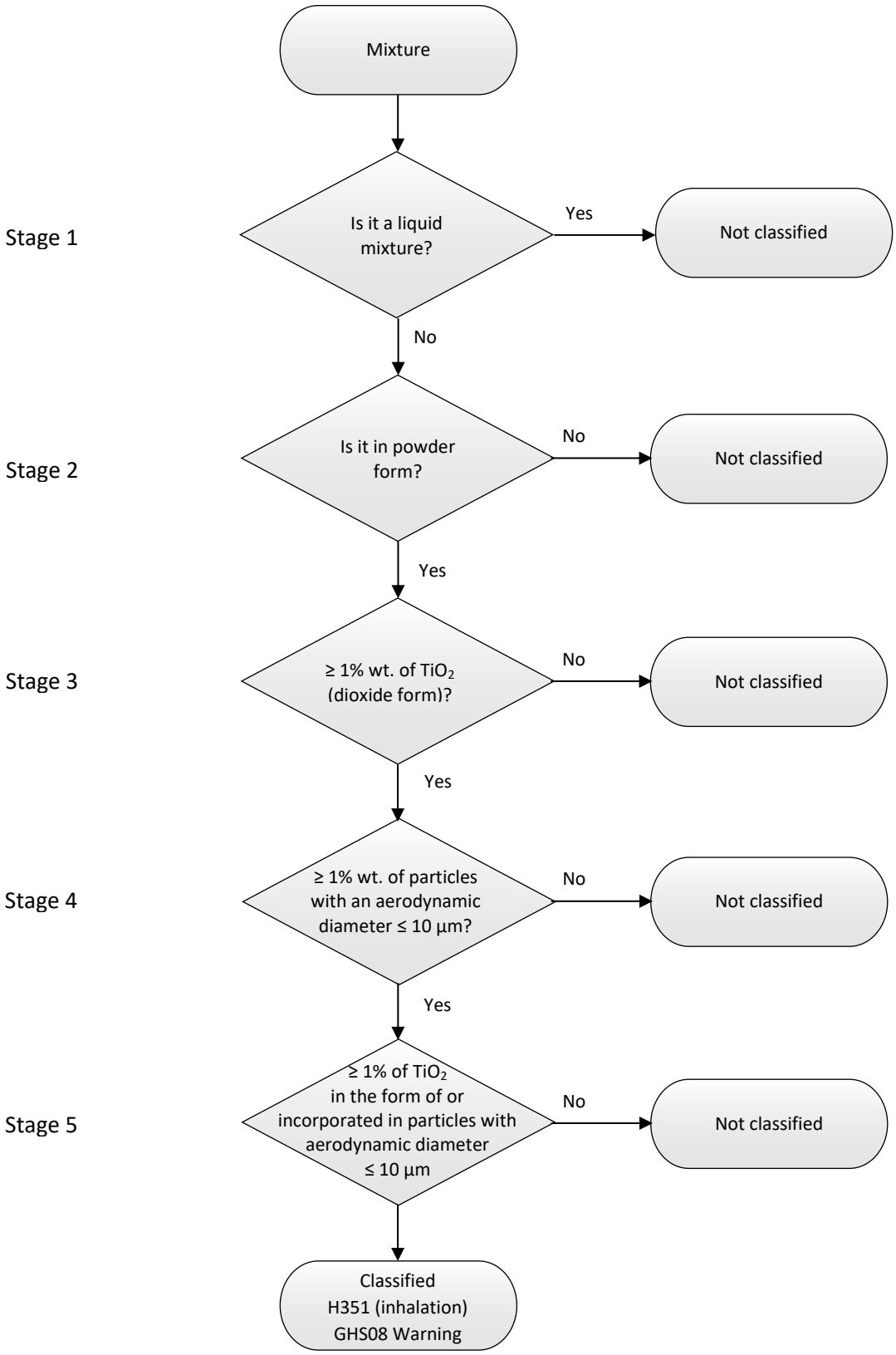


Figure 2: Decision tree for classification of mixtures showing the staged approach unless the mixture contains other hazardous substances.

3.9 Modified surface chemistry

Note V refers to substances placed on the market as particles with modified surface chemistry. Many types of TiO_2 are surface treated with chemicals to give properties such as decreased photocatalytic activity and improved dispersibility. The most common surface treatments are inorganic chemicals such as silica, alumina and zirconia and organics such as siloxanes or alkyl-silanes.

This interpretation considers that the vast majority of TiO_2 with modified surface chemistry falls within the same carcinogenic category 2 classification by inhalation and therefore are in the scope of the interpretation steps that it provides.

3.10 Fibres

Note V refers to substances placed on the market as fibres (with diameter < 3 µm, length > 5 µm and aspect ratio ≥ 3:1) or particles of the substance fulfilling the WHO fibre definition. This is a very rare form of TiO_2 and is not covered by this interpretation.

3.11 Sludges and pastes

This depends if they are considered a liquid or a solid. A liquid is defined in CLP as a substance or mixture which: (i) at 50°C has a vapour pressure of not more than 300 kPa (3 bar); (ii) is not completely gaseous at 20°C and at a standard pressure of 101,3 kPa; and (iii) which has a melting point or initial melting point of 20°C or less at a standard pressure of 101,3 kPa. A solid is defined as a substance or mixture which does not meet the definitions of liquid or gas. A powder is a solid therefore any sludge or paste not meeting the criteria of a liquid would not be classified. If the liquid criteria in CLP cannot be determined, then it can still be considered to be not classified if it is not a powder.

3.12 Articles

CLP only applies to substances and mixtures and not to articles and therefore articles such as plastic pipe or PVCu window frame that may contain more than 1%wt. of TiO_2 powder containing 1% or more of particles with aerodynamic diameter ≤ 10 µm do not require classification and labelling. Articles functioning as containers or carrier materials intended for releasing the substance still in a powder form may require labelling. Other requirements may apply under other EU legislation. See ECHA guidance on requirements for substances in articles.

4.0 Annex II – Special rules for labelling solid and liquid mixtures containing titanium dioxide

CLP includes the following new requirements for labelling of mixtures containing TiO_2.

Situation	Code	Label on packaging
Liquid mixtures containing 1 % or more of titanium dioxide particles with aerodynamic diameter equal to or below 10 µm	EUH211	Warning! Hazardous respirable droplets may be formed when sprayed. Do not breathe spray or mist.
Solid mixtures containing 1 % or more of titanium dioxide	EUH212	Warning! Hazardous respirable dust may be formed when used. Do not breathe dust.
Liquid and solid mixtures not intended for the general public and not classified as hazardous which are labelled with EUH211 or EUH212	EUH210	Safety data sheet available on request.
Mixtures not intended for the general public and not classified as hazardous, but which contain ≥ 0,1 % of a substance classified as carcinogenic category 2 (existing Annex II Section 2.10 requirement)		

TMDA considers that the obligation for extra labels on mixtures containing non-hazardous substances, as only certain forms of TiO_2 are hazardous, is legally questionable. However, this document is not meant to assess this.

4.1 Liquid mixtures

If the total content of TiO_2 in a liquid mixture is less than 1% wt., label EUH211 is not required.

If the total content TiO_2 is 1% wt. or more, the label is only required if the content of particles with an aerodynamic diameter ≤ 10 µm is 1% wt. or more. This is difficult to determine and may change from the TiO_2 powder used as an ingredient in the mixtures and therefore there is uncertainty related to the application of the EUH211 label. Due to this, some producers are conservatively applying the EUH 211 to liquid mixtures.

4.2 Solid mixtures

If the total content of TiO_2 in the solid mixture is less than 1% wt., label EUH212 is not required.

Classified solid mixtures in powder form containing 1% or more of TiO_2which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm require both the classification label H351 (inhalation) and label EUH212 (this was confirmed at the EU Advisory Committee for the Competent Authorities for REACH and CLP (CARACAL) on 4 May 2021.

4.3 TiO_2 Powder

It is not legally required to apply the EUH 212 label as TiO_2 powder is normally a substance and not a mixture. As many grades of TiO_2 do not meet the criteria for classification, many TiO_2 producers voluntarily apply the EUH 212 label to have communication down the supply chain.

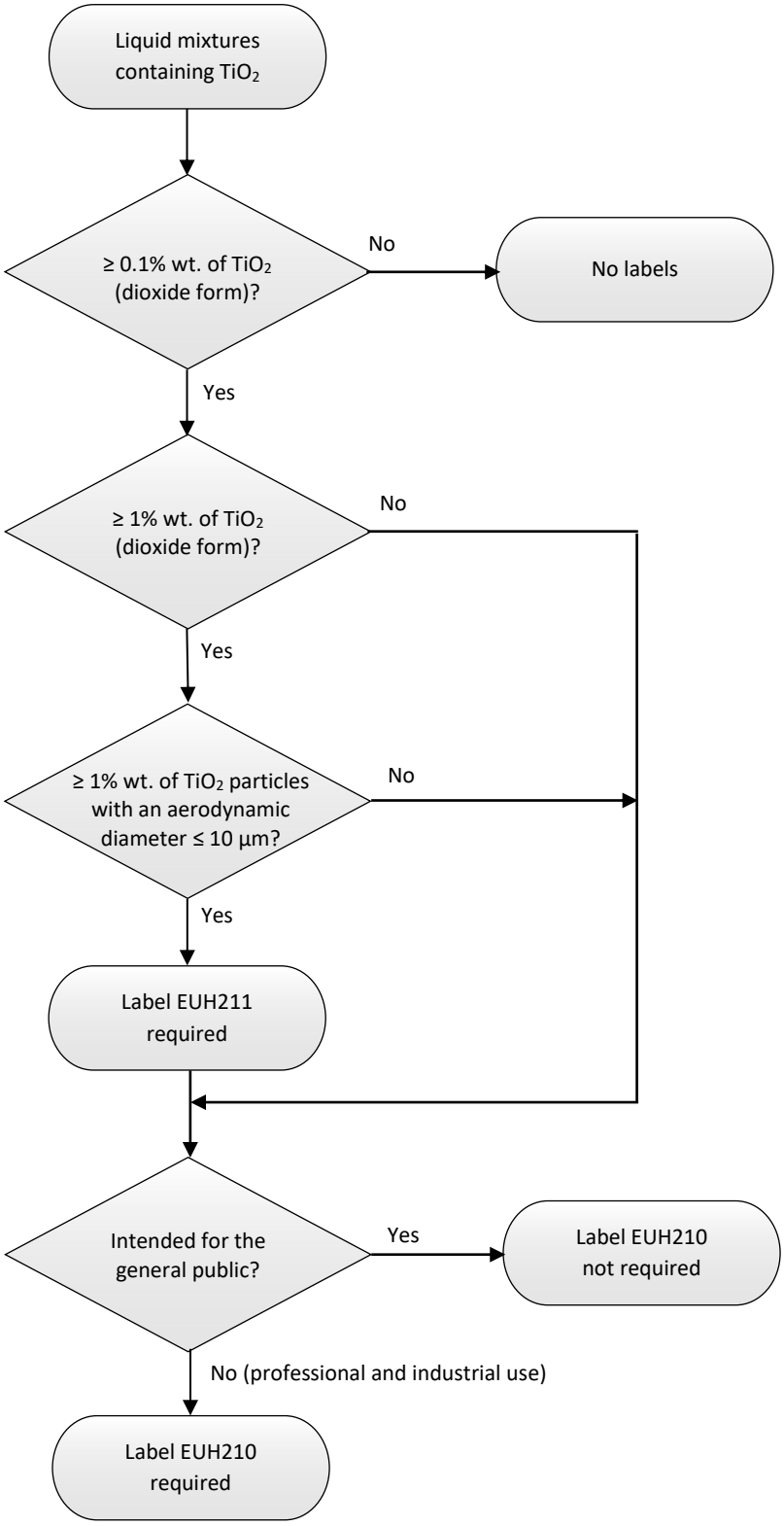


Figure 3: Decision tree for Annex II labelling of liquid mixtures unless the mixture contains other hazardous substances.

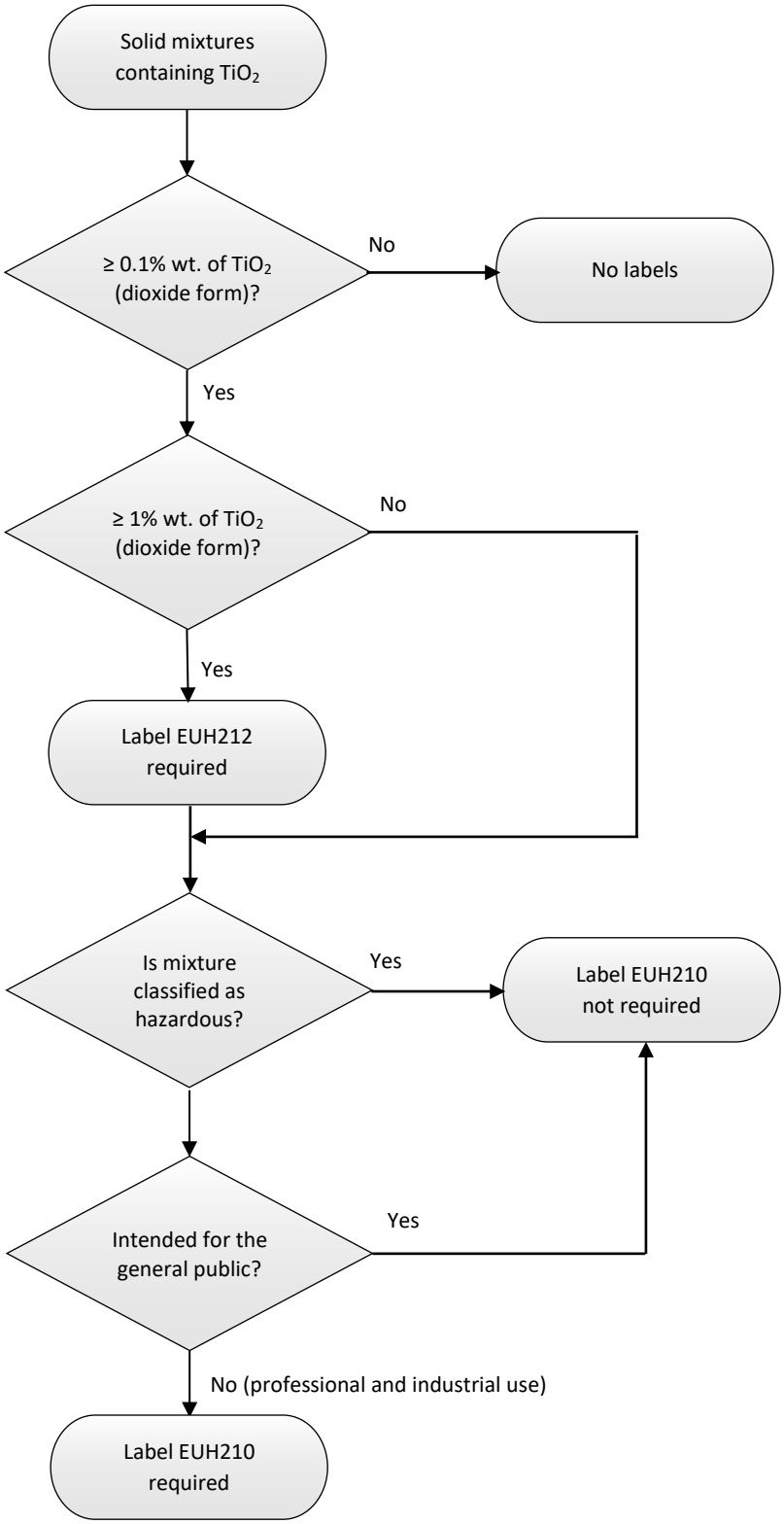


Figure 4: Decision tree for Annex II labelling of ≥solid mixtures unless the mixture contains other hazardous substances.

5.0 Determining the content of particles with aerodynamic diameter less than 10µm

5.1 Aerodynamic diameter

The classification specifically refers to the aerodynamic diameter which requires a specific type of measurement. It is used to determine the ability of particles suspended in air to reach the deep regions of the lung, the respirable fraction, and depends on the size, density and shape of particles. Larger more dense particles will settle out of the air at a higher velocity. The aerodynamic diameter was developed to determine the behavior of a particle in air, taking account of these factors and is illustrated in Figure 5.

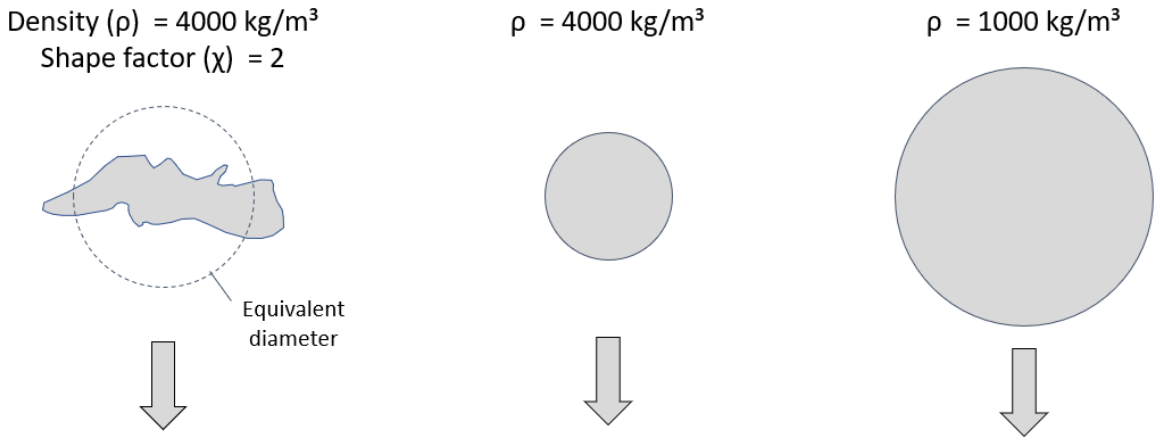


Figure 5: Principle of aerodynamic diameter.

The definition of aerodynamic diameter is included in the European Standard EN 481 on the size fraction definition of airborne particles in workplace as shown below.

The diameter of a sphere 1 g cm^{-3} with the same terminal velocity due to gravitational force in calm air, as the particle, under the prevailing conditions of temperature, pressure and relative humidity.

It is clear from this that to determine the aerodynamic diameter the measurement must be made in air, not by measuring the particle size distribution in a liquid dispersion. TiO_2 and solid mixtures containing TiO_2 are packaged in small or big bags (flexible intermediate bulk container (FIBC)) and therefore some suitable method for aerosolization which reflects expectable uses must be employed. The method should be standardized, easily available, reproducible, repeatable and correctly discriminate various materials and give directly amount of material below the threshold of 10µm aerodynamic diameter.

5.2 Determining the content of particles with aerodynamic diameter less than 10µm

As the aerodynamic diameter, must be determined in air, this guidance recommends determining the content of particles with an aerodynamic diameter ≤ 10 µm by carrying out a dustiness test to provide the aerosol to allow measurement of the aerodynamic diameter of the particles.

For TiO_2 powder, TDMA carried out an analytical project to review the suitability of available test methods. These are summarised in a separate TDMA Report TDMA1140j dated 21 April 2021 which showed EN 15051-2 Measurement of the dustiness of bulk materials - Rotating drum method provides the most consistent and repeatable results. This test is designed to mimic the dustiness of solid materials during typical handling and manipulation in a workplace and is illustrated in Figure 6. Other methods including EN15051-3 - Continuous drop method and DIN 55992-1, utilising the Heubach instrument were also shown to be robust and suitable for use.

This information was presented and reviewed a number of times including in the EU CARACAL meetings of 4 May 2021 and 30 June 2021. These are publicly available on the European Commission CIRCABC website. Even though there were some different views, the EU Commission concluded that this was with a fit for purpose and widely recognized method and no alternatives were proposed. TDMA are therefore recommending these methods.

Dustiness methods can depend on a number of factors such as humidity and some substances or mixture containing TiO_2 may have specific behavior and therefore the method may need to be adapted. This should be justified if it is used as the basis of classification.

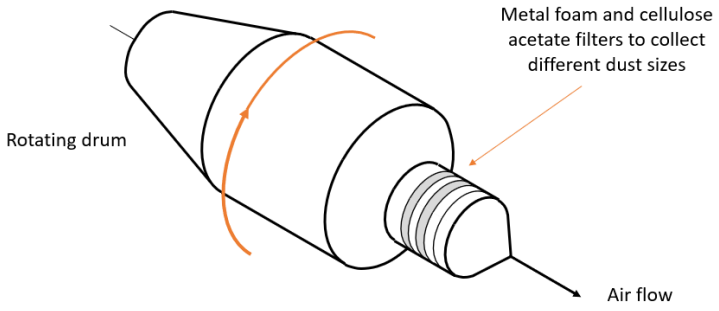


Figure 6: Principle of Measurement of the dustiness of bulk materials - Rotating drum method.

6.0 Safety datasheets (SDS)

The obligations depends on the position in the supply chain.

Case	Classification	Requirement
Manufacturer or importer		
TiO_2 powder containing **less than 1%** of particles with aerodynamic diameter ≤ 10 µm.	Non-hazardous substance	SDS (standard). Most suppliers are providing additional information on safe handling.
TiO_2 powder containing **1% or more** of particles with aerodynamic diameter ≤ 10 µm.	Hazardous substance	Extended safety datasheet (eSDS) with an annex of relevant exposure scenarios covering the uses.
TiO_2 powder mixture containing **1% or more** of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.	Hazardous mixture	eSDS with an annex of relevant exposure scenarios covering the uses - incorporating Annex II label info related to safe use in section 2.2 of the SDS - Warning! Hazardous respirable dust…….
Downstream – Formulator or distributor		
TiO_2 powder mixture **containing less than 1%** of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm	Non-hazardous mixture*	SDS (standard)
TiO_2 powder mixture containing **1% or more** of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.	Hazardous mixture	SDS (standard) Relevant information from the exposure scenarios of the hazardous ingredient substances should be communicated. Annex II label information related to safe use in should be included in Section 2.2 of the SDS - Warning! Hazardous respirable dust…….
TiO_2 liquid mixtures containing **1% or more** of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.	Non-hazardous mixture*	SDS (standard) Annex II label information related to safe use in should be included in Section 2.2 of the SDS - Warning! Hazardous respirable droplets ……
All		
TiO_2 liquid and solid including powder mixtures **containing 0.1% to less than 1%** of TiO_2 which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.	Non-hazardous mixture*	SDS (standard)

* Provided that there are no other hazardous substances that make the mixture hazardous.

REACH requires section 3 of the SDS to list information on hazardous ingredients, even if the mixture is non-hazardous.

Non-hazardous mixtures containing ≥ 0.1% by weight of carcinogen category 2 classified TiO_2 or containing at least one hazardous component exceeding the generic or specific concentration limit as specified in CLP, Annex II, paragraph 2.10, and not intended for the general public require label EUH210 - Safety data sheet available on request (see Section 4.0).

7.0 Theoretical examples for solids

To help illustrate the applicability, some simplified theoretical cases are shown in Table 1.

Basis: 10 particles only in two sizes; 20µm aerodynamic diameter (more than 10µm) and 5µm aerodynamic diameter (less than 10µm). Spherical with uniform density. Note that a 20µm particle has 64 x greater weight than a 5µm particle as it is a cubic relationship.

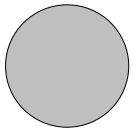
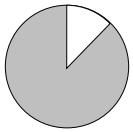
Case	Description	Number of 20µm particles with no TiO_2	Number of 20µm particles with 12% TiO_2	Number of 5µm particles with 12% TiO_2	Number of 5µm particles with 100% TiO_2	Total TiO_2 content	Percentage of particles less than 10µm	TiO_2 content of particles less than 10µm	Classified
									
						% wt.	% wt.	% wt.	
A	100% TiO_2 - Small particles only	0	0	0	10	100.0	100.0	100	Yes
B	12% TiO_2 evenly distributed, mostly large particles	0	8	2	0	12.0	0.39	0.05	No
C	12% TiO_2 evenly distributed, mostly small particles	0	2	8	0	12.0	5.9	0.71	No
D	Mix of small particles with 100% and 12% TiO_2	0	5	3	2	12.5	1.5	0.73	No
E	Mix of small particles with 100% and 12% TiO_2	0	5	1	4	13.1	1.5	1.27	Yes
F	Mix of small particles with 100% and 12% TiO_2	5	0	3	2	0.73	1.5	0.73	No

Table 1: Theoretical examples of classification of solids. The shaded cell indicates the basis of classification.

References

Commission Regulation (EC) No 1272/2008 on the classification, labelling and packaging (CLP) of substances and mixtures.

Commission Regulation (EU) 2020/217 adapting Regulation (EC) No 1272/2008 to technical and scientific progress (14th ATP).

European Chemical Agency (ECHA) (2017). Guidance on information requirements and chemical safety assessment Appendix R7-1 for nanomaterials applicable to Chapter R7a Endpoint specific guidance.

European Chemical Agency (ECHA) (2017). ECHA Guidance on requirements for substances in articles.

ECHA Guidance to Regulation (EC) No 1272/2008 on the classification, labelling and packaging (CLP) of substances and mixtures.

European Standards (1993) EN 481:1993, Workplace atmospheres. Size fraction definitions for measurement of airborne particles.

European Standards (2016) EN 15051-2 - Workplace exposure - Measurement of the dustiness of bulk materials - Part 2: Rotating drum method.

European Standards (2014) EN 15051-3 - Workplace exposure - Measurement of the dustiness of bulk materials - Part 3: Continuous drop method

German Institute for Standardization (2006). Determination of a parameter for the dust formation of pigments and extenders - Part 1: Rotation method. DIN 55992-1 - 2006-06

International Organization for Standardization. (2009). Particle size analysis — Laser diffraction methods (ISO Standard No. 13320

International Organization for Standardization. (2019). Powder metallurgy – Vocabulary (ISO Standard No. 3252)

TDMA (2021) TDMA1140j Harmonised classification and labelling of titanium dioxide (TiO_2), Content of particles with aerodynamic diameter ≤ 10 µm, Methods and results of analysis

About TDMA

The Titanium Dioxide Manufacturers Association (TDMA) is a sector group of the European Chemical Industry Council (Cefic) and represents the leading producers of titanium dioxide (TiO_2). TDMA is a non-profit organisation established in 1974 and dedicated to promoting the safe use and benefits of TiO_2 to society